

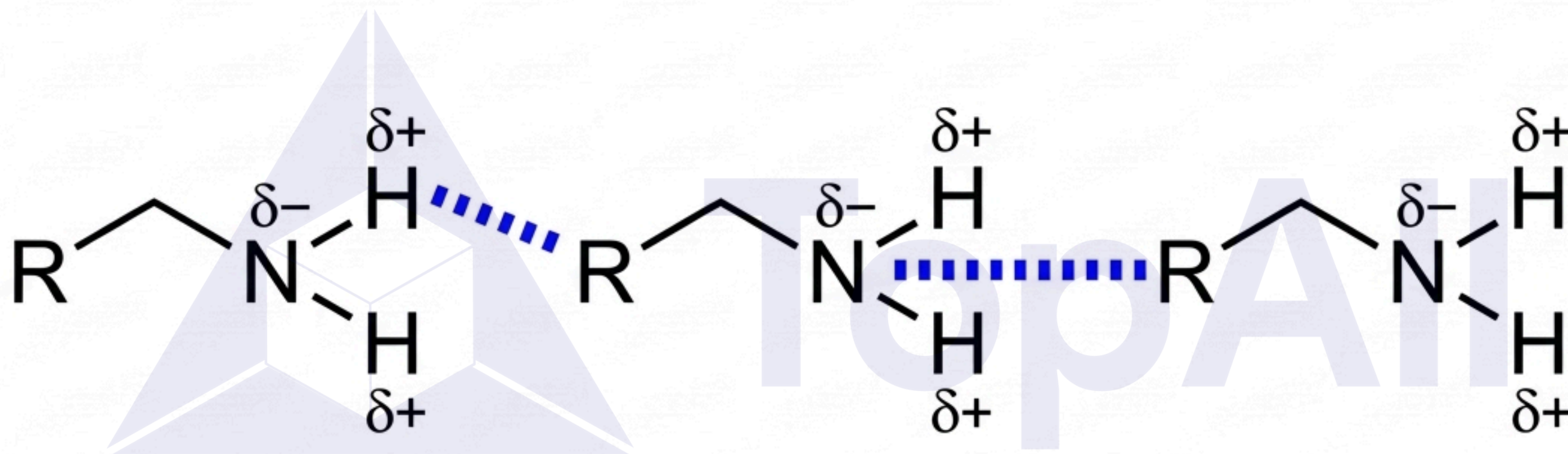
UNIT 9 • AMINES

Weightage: Medium

# 9.5 Physical Properties

Unpacking the structural drivers of boiling points, hydrogen bonding, and solubility.

# Intermolecular H-Bonding in Primary Amines



Primary and secondary amines associate via intermolecular hydrogen bonds, driving up their boiling points.

# How Amines Stack Up: The Boiling Point Ladder

| Compound                                       | Molar Mass | Boiling Point (K) | Relative B.P. |
|------------------------------------------------|------------|-------------------|---------------|
| $n\text{-C}_4\text{H}_{10}\text{H}$            | 74 g/mol   | 390.3K            | 100%          |
| $n\text{-C}_4\text{H}_9\text{NH}_2$            | 73 g/mol   | 350.8K            | 89.8%         |
| $(\text{C}_2\text{H}_5)_2\text{NH}$            | 73 g/mol   | 329.3K            | 84.3%         |
| $\text{C}_2\text{H}_5\text{N}(\text{CH}_3)_2$  | 73 g/mol   | 310.5K            | 79.5%         |
| $\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)_2$ | 72 g/mol   | 300.8K            | 77.0%         |



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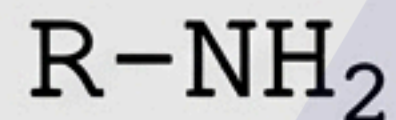
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# The H-Bond Factor in Isomeric Amines

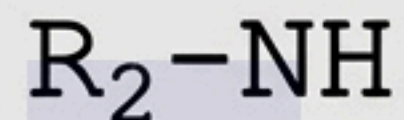
Primary (1°)



**2 N-H bonds**

Maximum intermolecular association. Highest boiling point among isomers.

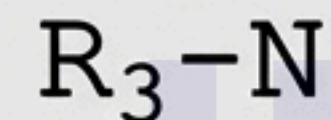
Secondary (2°)



**1 N-H bond**

Moderate intermolecular association. Medium boiling point.

Tertiary (3°)



**0 N-H bonds**

NO intermolecular H-bonding. Lowest boiling point.

# Electronegativity Dictates Strength

Nitrogen (N)

**Electronegativity = 3.0**

Weaker polar bonds,  
resulting in lower boiling  
points compared to alcohols  
of similar mass.

Oxygen (O)

**Electronegativity = 3.5**

Stronger polarization yields  
highly stable intermolecular  
hydrogen bonds, driving up  
the boiling point.

# The Hydrophobic Effect on Solubility

Lower Aliphatic Amines → Soluble

Higher Amines → Insoluble

Lower aliphatic amines dissolve readily in water due to their ability to form hydrogen bonds with  $\text{H}_2\text{O}$  molecules. However, as the molar mass increases, the size of the non-polar, hydrophobic alkyl chain grows. This bulky hydrocarbon tail disrupts the water's hydrogen-bonded network, causing higher amines to be essentially insoluble in water.

# Watch For This

## **The Trap:**

Assuming amines and alcohols of similar molar masses have identical physical properties.

## **The Reality:**

Because nitrogen (3.0) is less electronegative than oxygen (3.5), the N-H bond is less polar than the O-H bond. Consequently, amines always form weaker hydrogen bonds—and therefore have predictably lower boiling points and water solubility—than their corresponding alcohols.

# Section 9.5 Summary

- **Boiling Point Order:** Isomeric amines rank Primary > Secondary > Tertiary, directly correlating to the number of available N-H bonds.
- **Alcohols > Amines:** Due to Oxygen's higher electronegativity (3.5 vs 3.0), alcohols form stronger H-bonds and exhibit higher boiling points than comparable amines.
- **Solubility Drop-off:** Lower amines are water-soluble via H-bonding, but solubility plummets as the size of the hydrophobic alkyl part increases.

## Try 9.6 Chemical Reactions next →

Apply your knowledge of amine structure to basicity and nucleophilic reactions.



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